



Py-GC/MS studies and principal component analysis to evaluate the impact of feedstock and temperature on the distribution of products during fast pyrolysis

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ABSTRACT

This paper investigates the effect of pyrolysis temperature between 350 and 600 °C on the distribution of pyrolytic products derived from Avicel, α-cellulose, Douglas Fir wood (softwood) and Hybrid Poplar wood (hardwood) by Py-GC/MS as a way to identify the best conditions for bio-oil production. The products were grouped in five families depending on their origin. The C1 family is formed by products of cellulose fragmentation reactions (glycoaldehyde, acetol, 1,2-ethanediol, monoacetate, butanediol). The products grouped in the C2 family (levoglucosan, levoglucosenone, 1,4:3,6-dianhydro-α-D-glucopyranose) are derived from cellulose depolymerization reactions. The molecules derived from hemicellulose (acetic acid, furfural, 2-furanmethanol) were grouped in the H family. The products derived from lignin were grouped in two families L1 (derived from p-hydroxyl phenol (H) and guaiacyl (G) structures) and L2 (derived from syringyl (S) structures). Principal components analysis was used to identify the main factors controlling the distribution of products. Our results show that the yield of most of the pyrolytic products can be explained in the five groups or families described above. Most of the C1 products derived from Avicel, α-cellulose and Douglas Fir fragmentation reactions increase in yield as the temperature increases. In the case of Hybrid Poplar these products reach a maximum at 400 °C. CO₂, 2-oxo methyl ester propanoic acid, 1,2-cyclopentanedione, 3-methyl, levoglucosenone, 1,4:3,6-dianhydro-α-D-glucopyranose, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, and most of the phenolic compounds show a response to temperature changes that is independent of the feedstock processed. As the temperature increased the yield of levoglucosenone (product of dehydration reactions) decreased for all the samples studied. Levoglucosan yield is however highly dependent on the feedstock used and, as such, its behavior with temperature changes is more difficult to predict. The maximum yield of the products derived from lignin (L1 and L2) was found between 400 and 450 °C.

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1. Introduction

Global population growth and economic expansion is projected to lead to a 30% increase in world energy demand by 2040 [1]. Although fossil fuels are expected to remain the major source of energy, production growth is not expected to meet the increase in

demand [2]. The development of renewable and alternative energy sources is a primary concern for the countries with large land-mass such as Brazil and United States. Although there are many renewable sources to generate electricity, biomass is one of the few renewable sources capable of producing carbon based transportation fuels [3]. Lignocellulosic materials (consisting mainly of cellulose, hemicellulose, and lignin), are an abundant, renewable and low-cost organic resources [4]. The world annual estimated biomass production is 10–50 billion tons [4]. The use of lignocellulosic biomass for bio-fuel production can also reduce total greenhouse gas emissions [2,5,6].

Pyrolysis is an attractive technology able to convert up to 75% of the original biomass into a crude bio-oil that can be further refined

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Table 1

Cases studied in the PCA analysis.

Case	Biomass sample	Pyrolysis temperature (°C)	Case	Sample	Pyrolysis temperature (°C)
A	Avicel	350	M	Douglas Fir wood	350
B	Avicel	400	N	Douglas Fir wood	400
C	Avicel	450	O	Douglas Fir wood	450
D	Avicel	500	P	Douglas Fir wood	500
E	Avicel	550	Q	Douglas Fir wood	550
F	Avicel	600	R	Douglas Fir wood	600
G	α -Cellulose	350	S	Hybrid Poplar wood	350
H	α -Cellulose	400	T	Hybrid Poplar wood	400
I	α -Cellulose	450	U	Hybrid Poplar wood	450
J	α -Cellulose	500	V	Hybrid Poplar wood	500
K	α -Cellulose	550	W	Hybrid Poplar wood	550
L	α -Cellulose	600	X	Hybrid Poplar wood	600

for the production of fuels and chemicals. This process is typically conducted in the absence of oxygen at a temperature between 400 and 600 °C [3,7,8]. The organic fraction of bio-oil from pyrolysis has a gross heating value close to 22 MJ/kg. The actual heating value of crude oil depends on its water content which is related to the moisture of feedstock and process conditions [3]. Crude bio-oil can be economically transported for further refining 3–5 times further than raw biomass [3].

The quality of bio-oils is affected by the feedstock composition, particle size, pyrolysis conditions, feedstock moisture, ash content, among others [9–12]. In order to improve the quality of bio-oils, more selective pyrolysis reactors have to be developed. The development of selective pyrolysis reactors requires dependable analytical methods to study the distribution of products under different production conditions.

Many studies on the effect of pyrolysis temperature on the yield of products have been reported in the literatures [13–19]. However, apparent contradictory results have been reported. For example, He et al. [20], Garcia-Perez et al. [11], and Amutio et al. [21] have reported how pyrolysis temperature affects the yield of levoglucosan from three different feedstocks (Switchgrass, Mallee and Pinus insignis), respectively. He et al. found that the maximum yield of this compound is around 0.7 wt.% at 450 °C. Garcia-Perez et al. found that the maximum yield of this compound is around 4.2 wt.% at 425 °C. Amutio et al. [21] found that the maximum yield of this compound is around 2.09 wt.% at 500 °C. The analysis of the literature suggests that the effect of temperature on the yield of certain pyrolysis products is likely to be feedstock dependent.

Py-GC/MS is a useful analytical technique to characterize solid residues and to study the distribution of products resulting from the pyrolysis of lignocellulosic materials. This technique requires a very small amount of sample for examination and can be used to easily follow the evolution of pyrolysis products under different pyrolysis conditions [22]. The objective of this paper is to use Py-GC/MS together with principal component analysis (PCA) to evaluate the effect of pyrolysis temperature between 350 and 600 °C on the composition of vapors and to identify the products that are temperature dependent and feedstock independent.

2. Experimental

2.1. Biomass collection and characterization

The α -cellulose and the Avicel cellulose were purchased from Sigma–Aldrich. Douglas Fir wood was kindly supplied by Herman Brothers Logging in Port Angeles, WA. The Hybrid Poplar wood was collected at the Boise Cascade Corporation in Pasco, WA. The chemical composition (ash, extractives, cellulose, hemicelluloses, and lignin) of these samples was determined following ASTM standards and equivalent procedures recommended by NREL such as ASTM D1102-84 [23], D1105-96 [24], D1106-96 [25], E1758-01 [26].

Extractives were measured by soxhlet extraction using ethanol and toluene as solvents. The cellulose and hemicellulose contents were calculated by the mono-sugar content after a two-step sulfuric acid hydrolysis and analysis by ionic exchange chromatograph of the sugars obtained. Lignin content includes acid soluble and acid insoluble part. The acid soluble lignin was obtained by UV spectroscopy, and the acid insoluble lignin was calculated as the solid residues left after acid hydrolysis [13–15,25,27].

2.2. Reduction of alkali and alkaline earth metal (AAEM) and ICP-MS analysis

Alkali and alkaline earth metallic (AAEM) species (potassium, sodium, calcium and magnesium salts) are major constituents of woody biomass ash. These species are responsible for a drastic reduction in bio-oil yield. Thus, it is desirable to remove as much AAEM species as possible before pyrolysis [16]. The contents of alkaline metals in the samples were quantified by ICP-MS (Agilent Technologies-7500 Series) with an autosampler (Agilent Technologies-ASX-500 Series). 15 mg of ash samples were digested by 6 mL of concentrated reagent grade nitric acid (69–70%) at 90–95 °C for 2 h. Then, digested samples were diluted into 100 mL volumetric flasks with added 100 μ L of internal standard solutions (AccuStandard, Environmental Internal Standard Mix) for accuracy of further ICP analysis [28]. Calibration for each element is based on a standard solution (AccuStandard, Environmental Standard 1) with a 0.1% internal standard. The calibration curves were lines with R^2 values higher than 0.99 for all the elements tested.

2.3. Elemental analysis

Elemental analysis was performed using a LECO® TruSpec CHN instrument to identify the content of carbon, hydrogen, nitrogen, and oxygen. Ethylenediaminetetraacetic acid (EDTA) was used as standard. The method was corrected with a blank. Approximately 0.6 g of oven dry sample was wrapped in tin aluminum foil cups and burned for each test. The combustion process occurred at 950 °C in the combustion chamber with pure oxygen (99.993% high purity). Helium was used as carrier gas. All the tests were conducted in triplicates.

2.4. Py-GC/MS studies

The pyrolysis gas chromatography/mass spectrometer (Py-GC/MS) used in this study has a CDS pyroprobe 5000 connected directly to an Agilent GC/MS. An empty quartz tube with quartz wool was first cleaned at 1000 °C to make sure that all the gases and vapors adsorbed on the surface are removed. The samples were weighed with a thermogravimetric analyzer (0.5–0.7 mg), loaded into clear tubes, and kept in the oven at 280 °C for 1 min using 13.7 mL/min helium carrier gas to purge the oxygen in the

Table 2
Biomass composition (wt %).

Sample	Ash	Extractives	Acid insoluble lignin	Acid soluble lignin	Arabinose	Galactose	Glucose	Mann/xylose
Avicel	0.1	–	–	–	–	–	99.9	–
α -Cellulose	0.2	–	–	–	0.8	–	88.6	10.4
Douglas Fir	0.3	1.6	23.4	0.5	1.0	3.0	46.3	21.4
Hybrid Poplar	1.0	3.8	16.3	3.2	0.3	0.4	43.1	20.8

Table 3
Metal analysis of studied woody materials (ppm).

Sample	Na	Mg	K	Ca	Fe
Douglas Fir wood	1.94	82.56	83.02	484.8	3.74
Hybrid Poplar wood	22.47	320.46	322.40	1583.3	48.66

oven prior pyrolysis. Samples were pyrolyzed by heating the coil at approximately 800 °C/s to targeted temperatures of 350, 400, 450, 500, 550, and 600 °C. An Agilent 6890N equipped with a 30 m \times 0.25 mm inner diameter (5%-phenyl)-methylpolysiloxane non-polar column (HP5MS) was used to separate the compounds from pyrolysis gases and vapors. The GC/MS conditions were the following: inlet temperature at 250 °C, pressure 7.1 psi, split ratio 50:1. The oven temperature of the GC was held at 40 °C for 1 min followed by continuous heating (6 °C/min) to 280 °C with 1 mL/min helium carrier gas. Then, the final temperature was held for 15 min to ensure that no heavy molecules remained in the column. The mass spectrometer conditions used were: transfer line temperature 150 °C, ion source temperature 230 °C, and electron impact ionization (EI) at 70 eV. The NBS mass spectra library was used to identify the compounds in the chromatogram. Then, a semi-quantitative estimation of the yield of the compounds identified was calculated by dividing the desired peak areas by the mass of biomass pyrolyzed. All the tests were conducted in triplicates. In this paper the mean and the error bars (confidence intervals) were plotted. The confidence intervals were calculated multiplying the standard deviation by 1.687. This factor corresponds to a 90% of confidence for samples in triplicates (df: 2). The MS Excel polynomial curve fitting was used to plot the trend lines in most figures. Manual curve fitting was employed in cases in which the MS Excel polynomial curve fitting resulted in more than one peak without physical meaning.

2.5. Principal component analysis (PCA)

Principal component analysis (PCA) was used to identify the main factors affecting the yield of products obtained by Py-GC/MS. The PCA was conducted for 24 cases identified in Table 1 from A to X. In this analysis the number of principal components should be equal or less than the number of variables, in such a way that the first principal component has the largest possible variance and each succeeding component in turn has the highest variance possible under the restriction that it be orthogonal to the preceding components. Thus, a matrix considering cases-by-variables data (see Table 1), where each case represents a combined data of biomass kind \times pyrolysis temperature and the semi-quantitative estimation of the yield of each compound, was prepared. The PCA was then carried out using statistical software “Statistica” 8.0 at 95% confidence level [29].

Table 4
Elemental analysis (wt.%).

Biomass kind	C	H	N	Ash	O ^a
Douglas Fir wood	49.85 \pm 0.27	7.24 \pm 0.02	0.12 \pm 0.01	0.3	42.49 \pm 0.30
Hybrid Poplar wood	49.84 \pm 0.32	7.37 \pm 0.07	0.06 \pm 0.01	1.0	41.73 \pm 0.37

^a Value determined by difference. (Error estimated considering a 90% confidence interval out of triplicated samples).

3. Results and discussions

3.1. Biomass collection and characterization

The chemical composition of all the lignocellulosic materials studied is shown in Table 2. The results reported are in good agreement with typical values reported in the literature [30]. The choice of different biomass was made based on their contrasting chemical composition. Avicel, is a cellulose (crystallinity: 67%) in the form of fine powder derived from wood pulp by partial acid hydrolysis and spray drying of the washed pulp slurry (FMC BioPolymer, USA) with very little content of ash. The α -cellulose contains some hemicelluloses (xylan) and low content of ash. Douglas Fir and Hybrid Poplar Woods are forest biomasses that contain cellulose, hemicelluloses and lignin as well as ash (see composition in Table 2). Metal concentrations obtained by ICP-MS are listed in Table 3.

3.2. Elemental analysis

The elemental compositions of woody materials are shown in Table 4. The difference in elemental composition between softwood (Douglas Fir wood) and hardwood (Hybrid Poplar wood) is very small. The errors bars were calculated multiplying the standard deviation of triplicate measurements by 1.687 (confidence 90%).

3.3. Py-GC/MS studies to evaluate the effect of pyrolysis temperature

Figs. 1 and 2 show examples of Py-GC/MS chromatographs for the materials studied (Avicel, α -cellulose, Douglas Fir and Hybrid Poplar) at pyrolysis temperatures between 350 and 600 °C. The names of the molecules identified by NBS mass spectra library, the retention times, formulas, and the molecular weights are shown in Table 5. The analysis of pyrolysis products was carried out by groups.

Products derived from cellulose were divided in two families: C1 and C2. The peaks associated to C1 (carbon dioxide, hydroxyl-acetaldehyde and 1-hydroxy-2-propanone, cyclopentene derivatives, etc.) have between one and four carbon atoms. C2 compounds are produced from cellulose depolymerization reactions (levoglucosan, levoglucosenone), which have six carbon atoms.

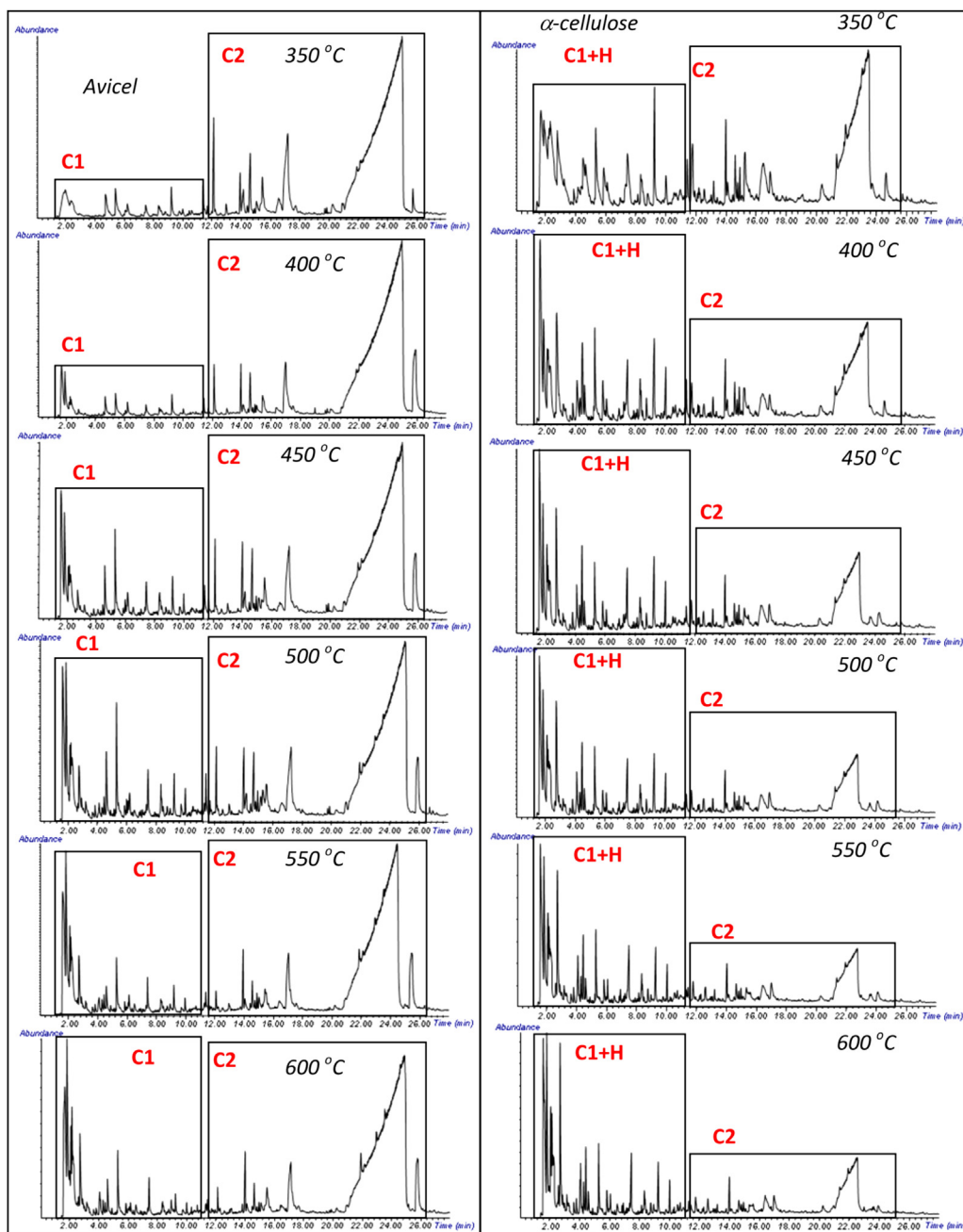


Fig. 1. Py-GC/MS chromatograms (Avicel and α -cellulose) at different pyrolysis temperatures.

The products of hemicellulose were all analyzed as a single group formed by acetic acid and furan derived compounds. Lignin derived compounds were also analyzed as two groups (L1 and L2) formed by molecules with between 7 and 11 carbon atoms. The compounds grouped in family L1 are derived from guaiacyl (G) and p-hydroxyl phenol (H) units. The compounds in family L2 are derived from syringyl units (S). The compounds associated to each of these groups are indicated by squares in Figs. 1 and 2.

A visual inspection of the chromatograms from 500 °C (Fig. 1) clearly shows that the main product from the pyrolysis of Avicel is levoglucosan. Significant amounts of levoglucosan were also obtained with α -cellulose (material containing cellulose and hemicelluloses). However, the production of levoglucosan (Fig. 2) was drastically reduced for materials containing lignin (Douglas Fir and Hybrid Poplar).

3.4. Principal component analysis (PCA)

Principal component analysis (PCA) is a technique that has been used to analyze the large data set obtained by Py-GC/MS [31–33]. The main goal of the principal component analysis was to identify the main factors governing the distribution of pyrolysis products in the four samples studied. The plot shown in Fig. 3 contains the factor scores for pyrolysis biomass samples at several temperatures (350–600 °C), with respect to the first two principal components (Factor I vs Factor II). It can be seen that the first two principal components accounted together for 72.52% of the total variance. The factors are influenced by the biomass studied. The samples with high cellulose content correlate positively with PC1.

Our result suggests that the behavior of the samples can be well understood if the composition of the samples is known. The

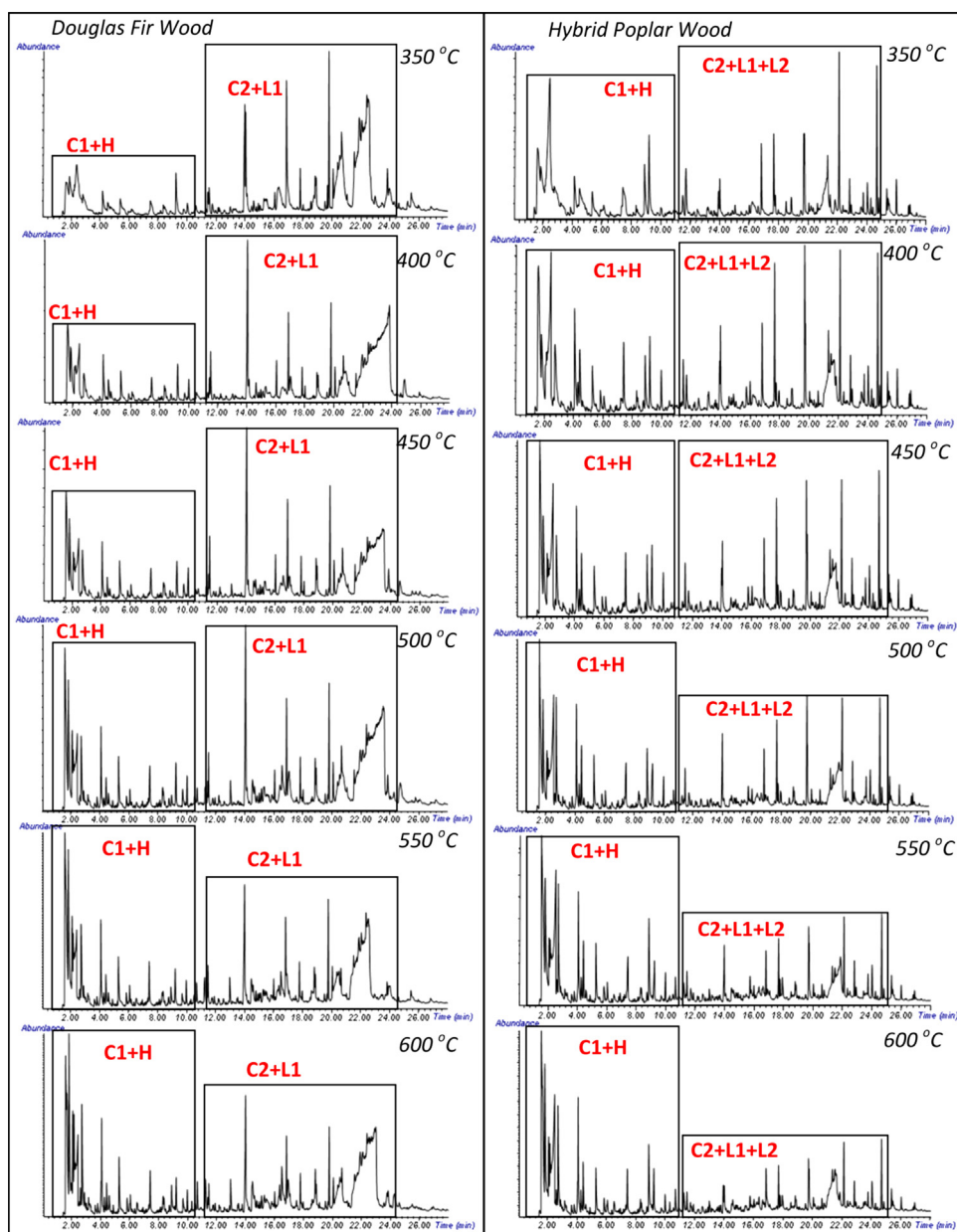


Fig. 2. Py-GC/MS chromatograms (Douglas Fir wood and Hybrid Poplar wood) at different pyrolysis temperatures.

samples were clustered into four different groups that correspond to the four biomasses studied. Avicel and α -cellulose are very similar in composition and, therefore in the PCA graph these groups were close. The Douglas Fir and Hybrid Poplar samples could be easily grouped in two groups. The samples correlating more strongly with PC1 tend to have higher contents of cellulose and lower contents of ash. The samples correlating the most with PC2 are Douglas Fir samples. According to Table 1 these samples have the highest content of acid insoluble lignin and galactose. Furthermore, all the samples pyrolyzed at the lowest pyrolysis temperatures (350 °C) seem to correlate positively with PC1 (see cases A, G, M and S).

The plot of loading factors is shown in Fig. 4. This plot can be used to visualize the relationship between the principal components PC1 and PC2 and the pyrolytic chemicals formed. The numbers inside the graph correspond to peak number listed in Table 4. Noticeable amount of clustering among the formed products is observed with a strong relationship to the groups created from the analysis of the

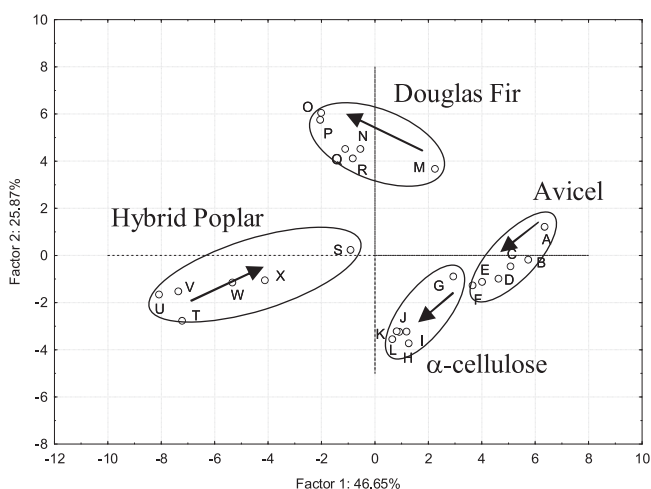
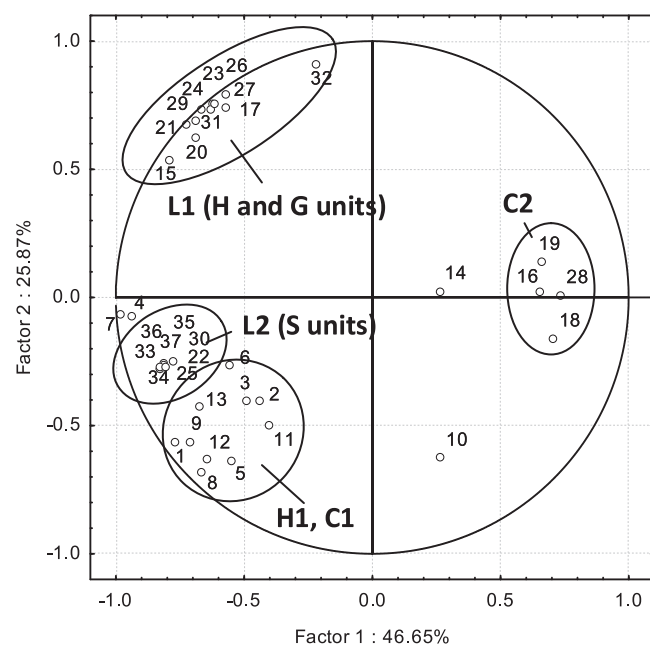
Py-GC/MS chromatographs. The chemicals products were found to group in four major clusters: (1) C2; (2) L1 (H and G units), (3) L2 (S units) and (4) C1-H.

Thus, a direct correlation between the yield of products and the starting sample was observed. For example the yields of levoglucosan, levoglucosenones and other products derived from cellulose depolymerization reactions were found to positively correlate with PC1 which was associated with samples containing a high content of cellulose and a low content of ash. The phenolic compounds with one methoxyl group (G units) correlated positively with PC2 which is associated with Douglas Fir (a softwood containing these compounds). The products of cellulose and hemicellulose fragmentation reactions (C1, H) and the phenolic compounds with two methoxyl groups (S units) (L) correlate negatively with PC1 and PC2. These components were also associated to the Hybrid Poplar which is the feedstock with the highest ash content and a lignin containing the highest fraction of syringyl alcohol units.

Table 5

Main products used in the quantification of Py-GC/MS spectra.

Peak no	Name of compound	Retention time (min)	Formula	m/z	MW	Feedstock found	Source
1	Carbon dioxide	1.587	CO ₂	44	44	All	C, H, L
2	2-Oxo-propanoic acid (isopropenyl acetate)	1.8	C ₃ H ₄ O ₃	43	88	Hemicellulose	H
3	Glycolaldehyde	2.107	C ₂ H ₄ O ₂	32	60	All	C1
4	Acetic acid	2.458	C ₂ H ₄ O ₂	45	60	Hemicellulose	H
5	1-Hydroxy-2-propanone, (Acetol)	2.745	C ₃ H ₆ O ₂	43	74	All	C1
6	3-Methyl-furan	3.818	C ₅ H ₆ O	82	82	All	C1
7	Monoacetate-1,2-ethanediol	4.1	C ₄ H ₈ O ₃	43	104	All	C1
8	Butanedial	4.34	C ₄ H ₆ O ₂	58	86	All	C1
9	2-Oxo-, methyl ester-propanoic acid	4.506	C ₄ H ₆ O ₃	43	102	All	C1
10	Furfural	5.339	C ₅ H ₄ O ₂	96	96	All	H
11	2-Furanmethanol	5.777	C ₅ H ₆ O ₂	41	98	Hemicellulose	H
12	2-Hydroxy-2-cyclopenten-1-one	7.447	C ₅ H ₆ O ₂	98	98	All	C1
13	3-Methyl-1,2-cyclopentanediol	9.914	C ₆ H ₈ O ₂	112	112	All	C1
14	2,5-Dimethyl-4-hydroxy-3(2H)-furanone	11.321	C ₆ H ₈ O ₃	43	128	All	C1
15	2-Methoxy-phenol	11.578	C ₇ H ₈ O ₂	109	124	DF ^a + HP ^b	L1, L2
16	Levoglucosenone	12.162	C ₆ H ₆ O ₃	98	126	All	C2
17	2-Methoxy-4-methyl-phenol	14.121	C ₈ H ₁₀ O ₂	123	138	DF + HP	L1, L2
18	1,4:3,6-Dianhydro-α-D-glucopyranose	14.56	C ₆ H ₈ O ₄	69	144	All	C2
19	5-Hydroxymethyl-2-furancarboxaldehyde	15.3	C ₆ H ₆ O ₃	97	126	All	C2
20	4-Ethyl-2-methoxy-phenol	15.967	C ₉ H ₁₂ O ₂	137	152	DF + HP	L1, L2
21	2-Methoxy-4-vinylphenol	16.942	C ₉ H ₁₀ O ₂	135	150	DF + HP	L1, L2
22	2,6-Dimethoxy-phenol	17.771	C ₈ H ₁₀ O ₃	154	154	DF + HP	L1, L2
23	Eugenol	17.891	C ₁₀ H ₁₂ O ₂	164	164	DF + HP	L1, L2
24	Vanillin	18.879	C ₈ H ₈ O ₃	151	152	DF + HP	L1, L2
25	4-Methoxy-3-(methoxymethyl)-phenol	19.69	C ₉ H ₁₂ O ₃	168	168	HP	L2
26	2-Methoxy-4-(1-propenyl)-, (E)-phenol	19.785	C ₁₀ H ₁₂ O ₂	164	164	DF + HP	L1, L2
27	2-Methoxy-4-propyl-phenol	19.992	C ₁₀ H ₁₄ O ₂	137	166	DF + HP	L1, L2
28	Levoglucosan	20.502	C ₆ H ₁₀ O ₅	60	162	All	C2
29	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	21.463	C ₁₀ H ₁₂ O ₃	137	180	DF + HP	L1, L2
30	3',5'-Dimethoxyacetophenone	22.227	C ₁₀ H ₁₂ O ₃	165	180	HP	L2
31	4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	22.304	C ₁₀ H ₁₂ O ₃	137	180	DF + HP	L1, L2
32	4-Hydroxy-3-methoxy-benzeneacetic acid	23.818	C ₉ H ₁₀ O ₄	137	182	DF + HP	L1, L2
33	4-Hydroxy-3,5-dimethoxy-benzaldehyde	23.964	C ₉ H ₁₀ O ₄	182	182	HP	L2
34	2,6-Dimethoxy-4-(2-propenyl)-phenol	24.789	C ₁₁ H ₁₄ O ₃	194	194	HP	L2
35	1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone	25.311	C ₁₀ H ₁₂ O ₄	181	196	HP	L2
36	Desaspidinol	25.962	C ₁₁ H ₁₄ O ₄	167	210	HP	L2
37	3,5-Dimethoxy-4-hydroxycinnamaldehyde	29.534	C ₁₁ H ₁₂ O ₄	208	208	HP	L2

^a DF: Douglas Fir.^b HP: Hybrid Poplar.**Fig. 3.** Score plot of principal components for four biomasses pyrolyzed at different temperatures.**Fig. 4.** Loading plots of factor 1 (PC1) and factor 2 (PC2) for model with all the compounds.

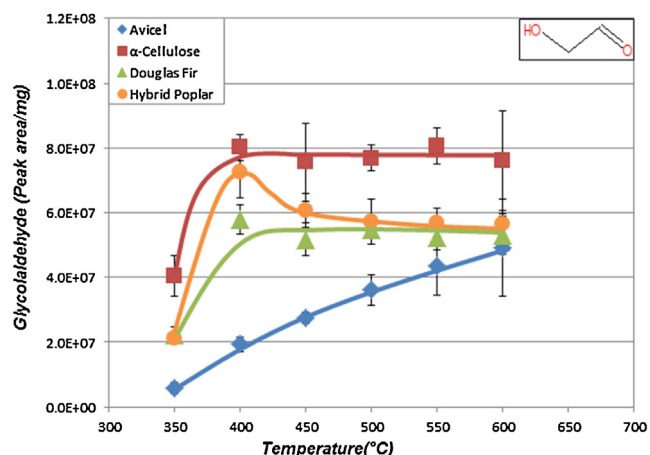


Fig. 5. Effect of pyrolysis temperature on the peak area/mg of glycolaldehyde.

3.5. Effect of pyrolysis temperature on the distribution of products of cellulose (families C1 and C2)

Fig. 5 shows the effect of pyrolysis temperature on the glycolaldehyde (hydroxyacetaldehyde) formation. The semi-quantitative yield estimation was expressed as peak area divided by sample weight in mg. This compound is formed from cellulose fragmentation reactions. In the case of Avicel, the yield increases as the pyrolysis temperature increases, similar to the results reported by Shen [34] and Liao [35]. In this context, Liao [35] concluded that the yield of hydroxyacetaldehyde increases with the temperature for cellulose pyrolysis. Avicel resulted in a lower yield of hydroxyacetaldehyde than other feedstocks, likely due to the low content of ash in this sample as the alkalis contained in the ash are known to catalyst cellulose fragmentation reaction [36,37]. For α-cellulose and woody biomass, the fragmentation reactions increase with pyrolysis temperatures up to 400 °C, but show no significant changes with temperatures over 400 °C. The highest yield of

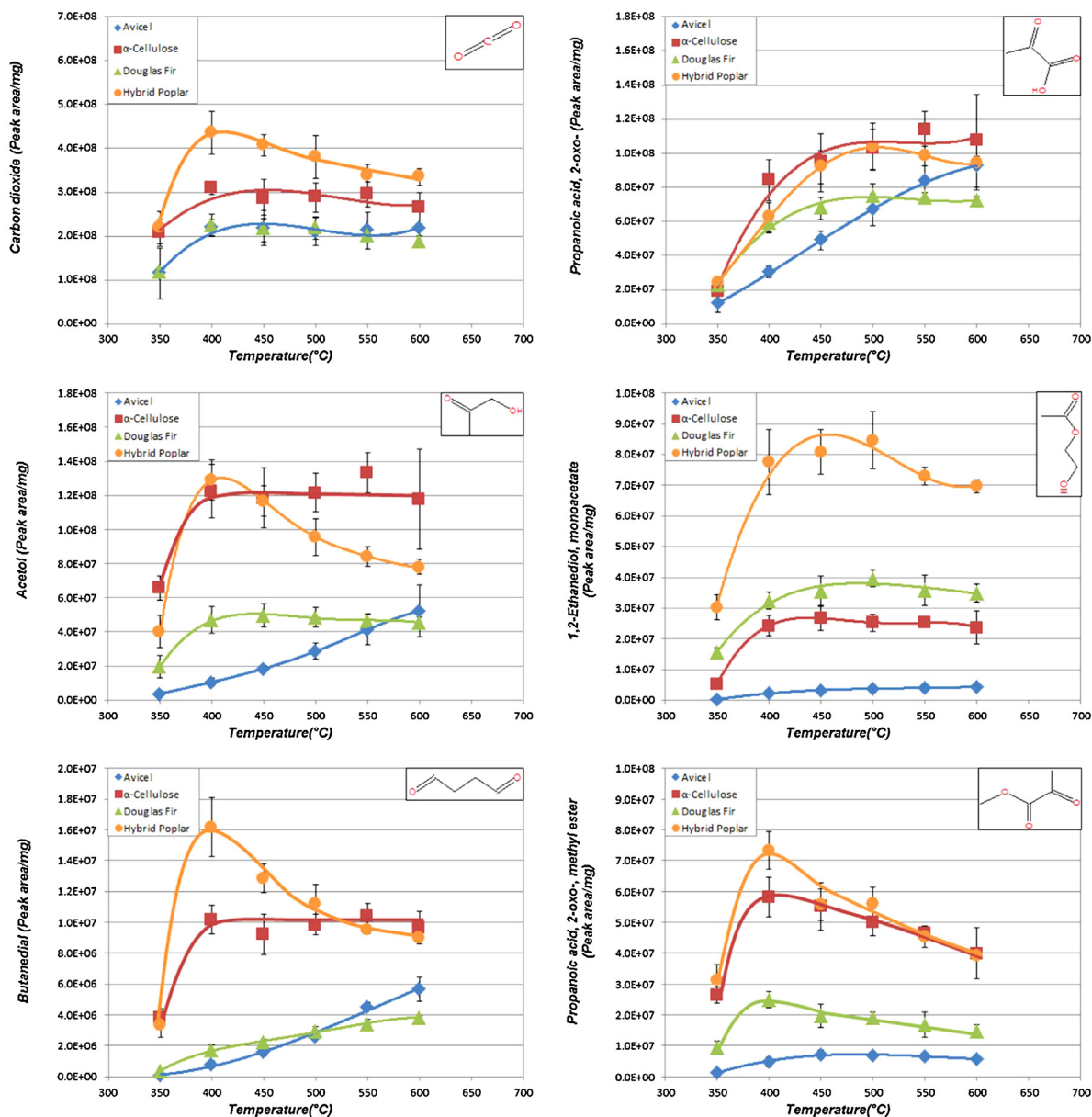


Fig. 6. Effect of pyrolysis temperature on the peak area/mg of molecules with less than four carbon atoms.

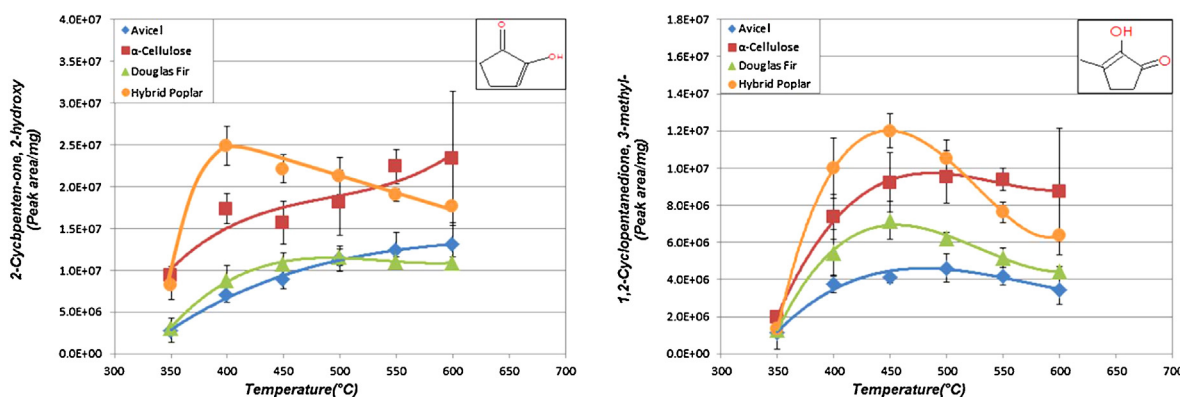


Fig. 7. Effect of pyrolysis temperature on the semiquantitative estimation of the yield of 2-hydroxy-2-cyclopenten-1-one and 3-methyl-1,2-cyclopentanedione.

glycoaldehyde was obtained for α -cellulose. This result can likely be explained by the high content of cellulose and the presence of sufficient alkaline matter to catalyze the fragmentation reactions. The interactions between cellulose and xylose cannot be ruled out as a factor affecting the formation of this compound.

Fig. 6 shows the effect of pyrolysis temperature on the formation of other C1 molecules including; carbon dioxide, 2-oxo-propanoic acid, acetol, 1,2-ethanedial, monoacetate, butanedial, 2-oxo methyl ester, propanoic acid. CO_2 is a fragmentation product from the degradation of each bio-polymer forming the biomass. In all samples, the production of CO_2 increases as the pyrolysis temperatures increases and reaches a plateau at 400 °C. As the temperature increases further CO_2 formation decreases slightly. This behavior is in agreement with the results reported by Wang et al. [38] for the pyrolysis of beech wood. For most molecules with less than four carbon atoms it is observed that their yields are maximized near 400 °C. This maximum is more pronounced in the case of Hybrid Poplar. In the case of 2-oxo propanoic acid, the maximum is achieved close to 450 °C. However for Avicel, the production does not plateau as the pyrolysis temperature increases and no significant maximum was observed for 2-oxo-propanoic acid, acetol or butanedial.

The molecules with five and six carbon atoms (2-hydroxy-2-cyclopenten-1-one and 3-methyl-1,2-cyclopentanedione) formed as a function of pyrolysis temperature are shown in Fig. 7. In this case, a moderate continuous increase in the yield of 2-hydroxy-2-cyclopenten-1-one with the pyrolysis temperatures was observed in most samples. A maximum of 3-methyl-1,2-cyclopentanedione production was only observed for Hybrid Poplar Wood at a pyrolysis temperature around 400 °C.

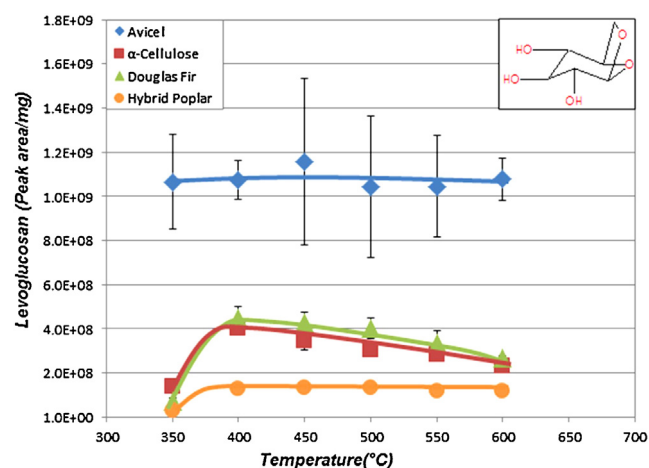


Fig. 8. Effect of pyrolysis temperature on the peak area/mg of levoglucosan.

The production of 3-methyl-1,2-cyclopentanedione increased and reached a maximum when the samples were pyrolyzed at 450 °C, with yields decreasing slightly as the pyrolysis temperatures increased. It is interesting to note that the production of these molecules significantly decreases at higher pyrolysis temperatures.

Fig. 8 shows the effect of pyrolysis temperature on levoglucosan (C2 family). Levoglucosan is the primary decomposition product from depolymerization reaction of cellulose. As mentioned earlier, Hybrid Poplar wood produces less levoglucosan compared with other samples due to the high ash content of the feedstock [39].

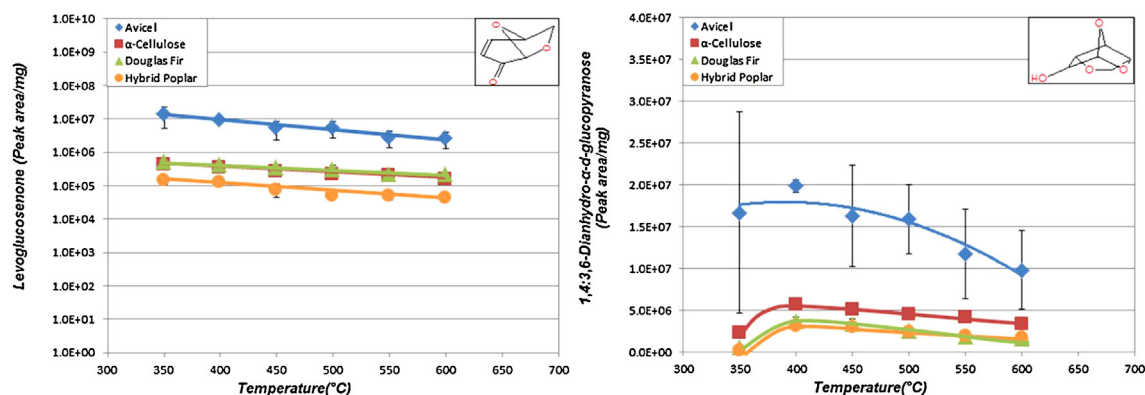


Fig. 9. Effect of pyrolysis temperature on minor C_6 sugars (levoglucosenone and 1,4:3,6-dianhydro- α -D-glucopyranose) formation expressed as peak area/biomass weight (mg).

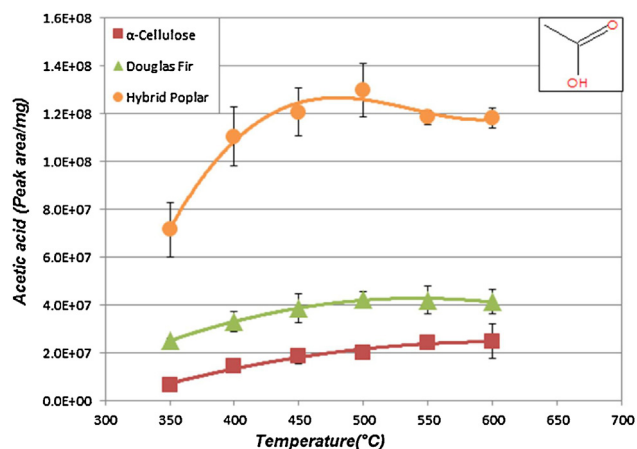


Fig. 10. Effect of pyrolysis temperature on formed acetic acid expressed as the peak area/biomass weight (mg).

Using Avicel, pyrolysis temperature was found to slightly reduce the yield of anhydrosugar levoglucosan in agreement with the results of Patwardhan [39]. All other samples were found to show a significant decrease in the yield of levoglucosan as the pyrolysis temperature over 400 °C.

Levoglucosenone and 1,4:3,6-dianhydro- α -D-glucopyranose can be formed by dehydration of levoglucosan [40]. Levoglucosenone is a minor sugar obtained from pyrolysis of cellulose. Higher productions of levoglucosenone can be observed at low pyrolysis temperatures. As the temperatures are increased, the production of levoglucosenone slowly decreased (Fig. 9). A possible cause of this reduction is more rapid volatilization of levoglucosan from the liquid intermediate. 1,4:3,6-dianhydro- α -D-glucopyranose is another minor sugar derived from pyrolysis of cellulose [41] and its reduction can be observed when the pyrolysis temperatures is increased over 400 °C (Fig. 9).

3.6. Effect of pyrolysis temperature on the distribution of products from hemicellulose (family H)

Fig. 10 shows the effect of pyrolysis temperature on acetic acid. Acetic acid is thought to be formed from the initial elimination of acetyl groups which are linked to the xylan chain on the C-2 position (glucomannan) related to hemicellulose [42]. The production of acetic acid increases by with pyrolysis temperature and reaches a plateau over 450 °C. Hybrid Poplar wood has higher yields of acetic acid than other samples. The production of furans with five carbon atoms increased with increasing pyrolysis temperatures up to temperatures of 400 °C. Behavior at higher temperatures became highly feedstock and product dependent with plateaus, increased and decreased yields all observed for furan products above 400 °C (Fig. 11). A similar result was reported by Amutio et al. [21] for Pinus insignis pyrolysis. The production of 2-furan methanol decreases (~82%) with increasing temperatures from 400 to 600 °C.

3.7. Effect of pyrolysis temperature on the distribution of products from lignin (family L1 and L2)

Figs. 13 and 14 show the effect of pyrolysis temperature on the production of phenolic compounds derived from lignin. Phenolic compounds are assigned to different groups on the basis of GC retention time. Fig. 12 shows that pyrolysis temperature dramatically affects the production of phenolic compounds (family L1) (2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenol and 2-methoxy-4-vinylphenol). A pyrolysis temperature of 450 °C seems to enhance the production of

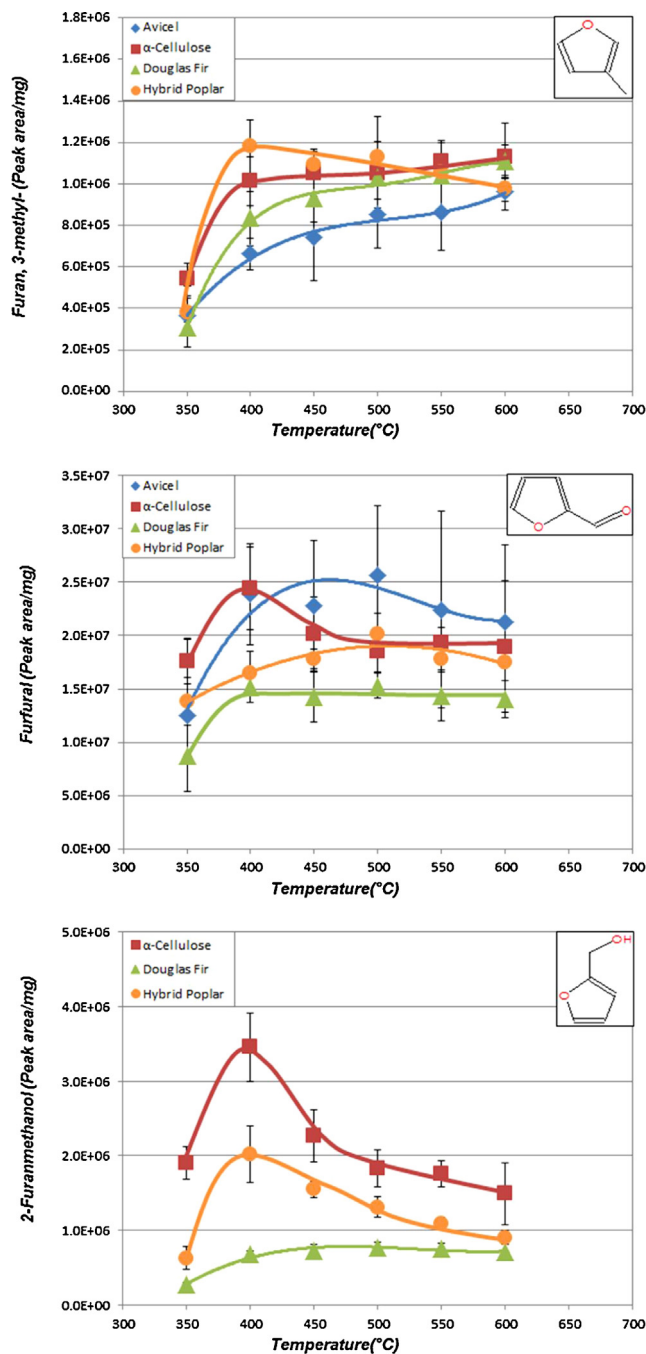


Fig. 11. Effect of pyrolysis temperature on formed furans with five carbon atoms (3-methyl-furan, furfural and 2-furanmethanol) expressed as the peak area/biomass weight (mg).

phenolic compounds. The results on 2-methoxy-phenol, and 2-methoxy-4-methyl-phenol, are in agreement with those obtained by Garcia-Perez et al. [11] for the maximum production at pyrolysis temperature around 425 °C.

Fig. 13 shows that pyrolysis temperature also affects the productions of eugenol, vanillin, 2-methoxy-4-(1-propenyl)(E)-phenol, and 2-methoxy-4-propyl-phenol. The production of these phenolic compounds increases with increasing pyrolysis temperatures and then slightly decreases over around 500 °C. A similar plateau (400–500) was observed by Garcia-Perez et al. [11] in Mallee wood pyrolysis.

Fig. 14 shows the effect of pyrolysis temperature on the production of phenolic compounds with a GC residence time 17–24 min

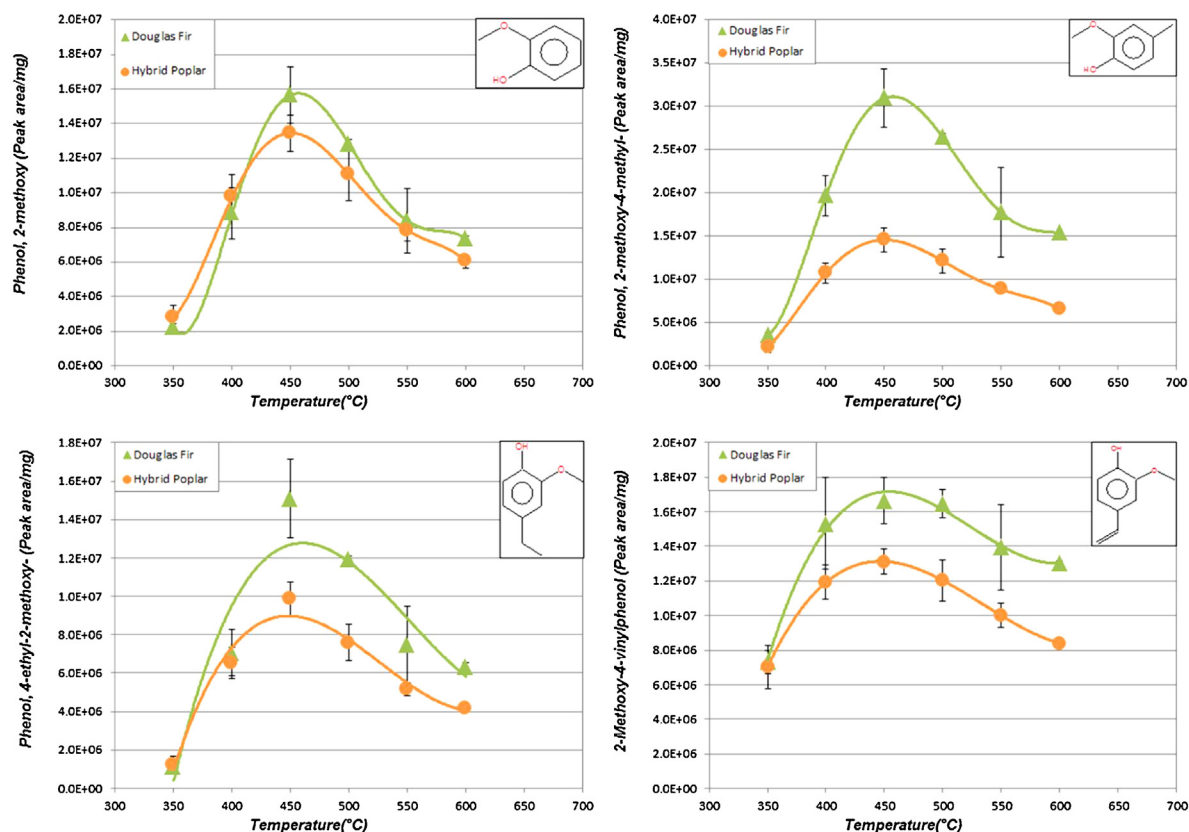


Fig. 12. Effect of pyrolysis temperature on the formed phenolic compounds (retention time between 11 and 17 min) expressed as peak area/biomass weight (mg).

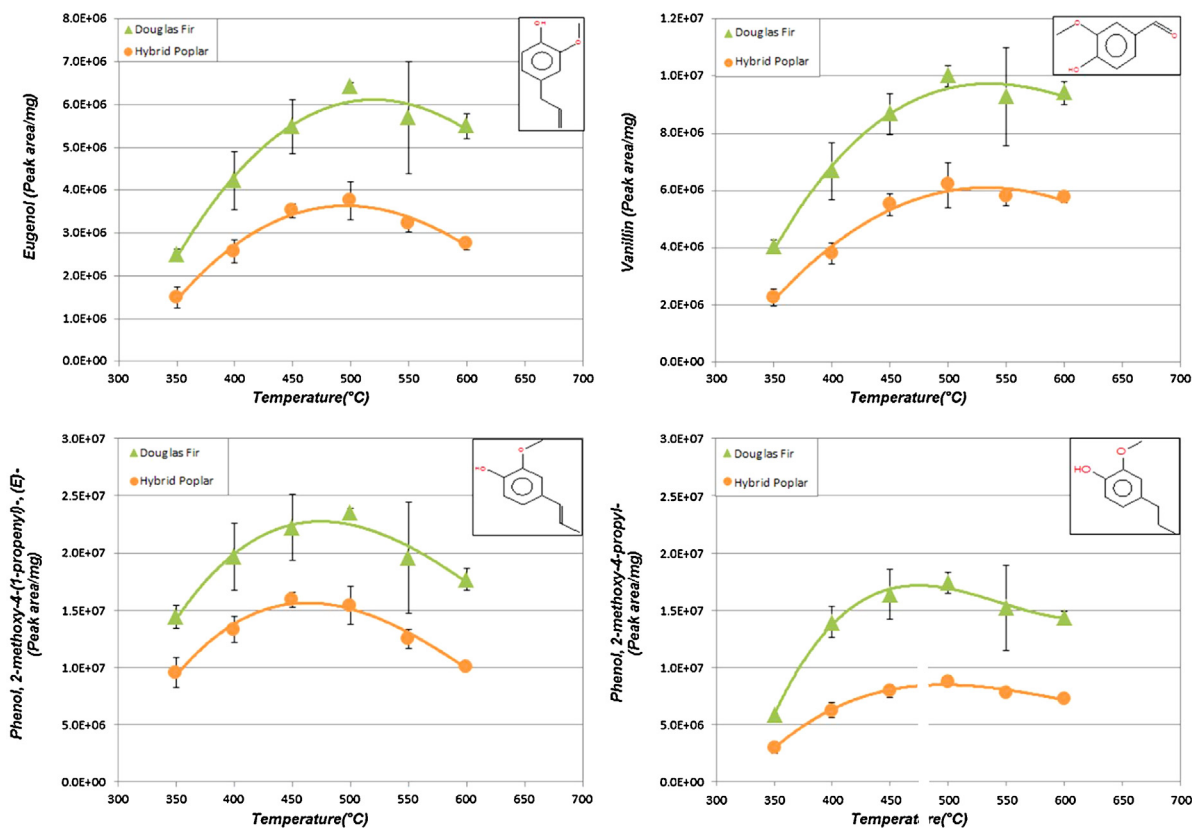


Fig. 13. Effect of pyrolysis temperature on phenolic compounds (retention time from 17 to 20 min) expressed as the peak area/biomass weight (mg).

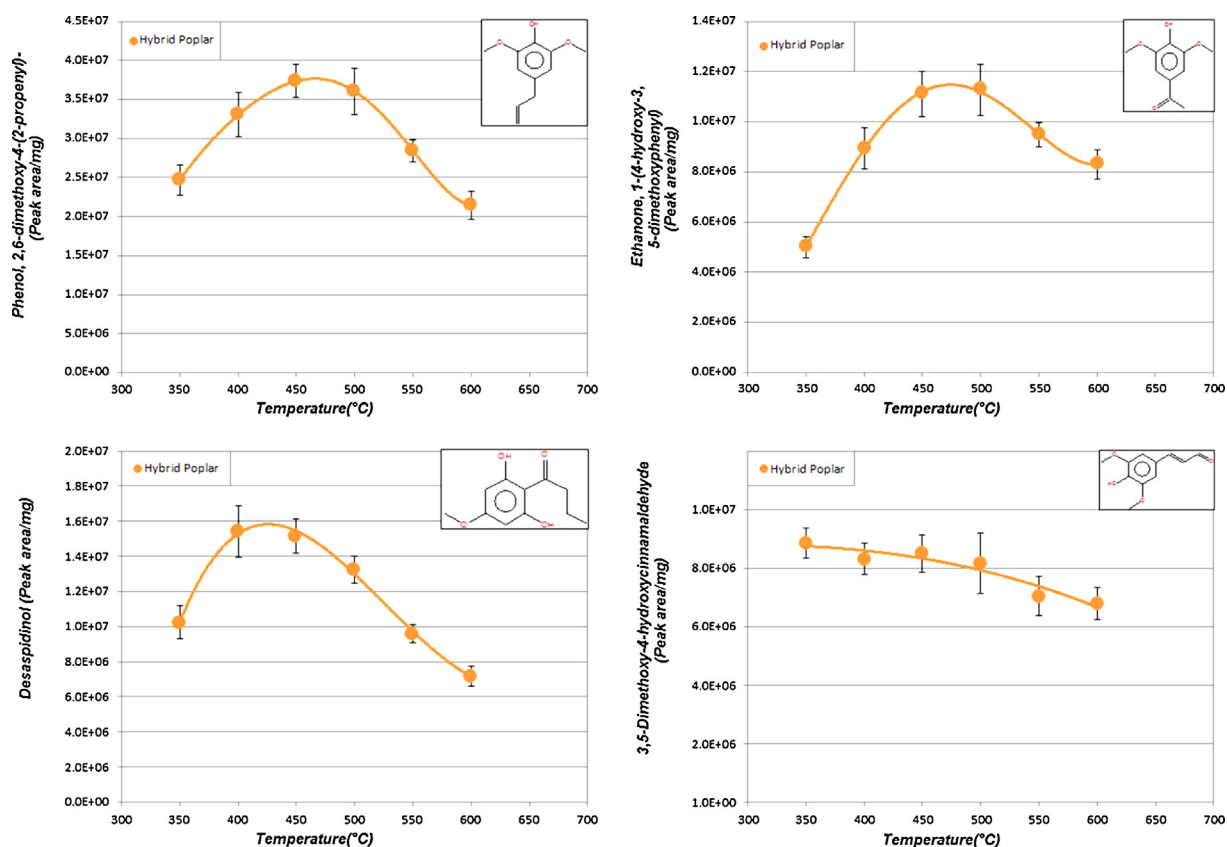


Fig. 14. Effect of pyrolysis temperature on the phenolic compounds derived from hardwood (retention time from 17 to 24 min) expressed as peak area/biomass (mg).

derived from hardwood (family L2) (2,6-dimethoxy-phenol, 4-methoxy-3-(methoxymethyl)-phenol, 4-hydroxy-3,5-dimethoxy-benzaldehyde, and 3',5'-dimethoxyacetophenone). The pyrolysis temperature seems to enhance the production of these phenolic compounds in the range of temperature between 350 and 450 °C. The drastic reduction in their production over 450 °C may be explained by the increase of secondary reactions as temperature increases [13].

4. Conclusions

The effect of pyrolysis temperature on the yield of products derived from the pyrolysis of Avicel, α-cellulose, Douglas Fir and Hybrid Poplar was investigated. Py-GC/MS analysis proved to be a powerful tool to discriminate the formation of the pyrolytic chemicals as a function, of both, biomass type and pyrolysis temperature. PCA shows that the pyrolysis products can be divided by groups and that their behavior is strongly influenced by the nature of the feedstock studied. It was found that CO₂, 2-oxo methyl ester-propanoic acid, 3-methyl-1,2-cyclopentanedione, levoglucosenone, 1,4:3,6-dianhydro-α-D-glucopyranose, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, and most of the phenolic compounds show a response to temperature changes that is independent of the feedstock processed. The rest of the compounds, however, are highly dependent on the feedstock used and, as such, their behaviors are more difficult to predict. This dependency on the feedstock suggests that strong interactions between the biomass constituents occur during pyrolysis. The results reported in this paper should be analysed carefully taking into account that only a relatively small fraction of the pyrolysis products are detectable by GC/MS. For lignocellulosic materials even with relatively low alkaline content (more than 0.1 wt.%) the fraction detectable by GC/MS is typically between 16 and 23 wt.% [11]. Higher GC/MS detectable fractions (up

to 60 wt.%) can be obtained when using acid washed cellulose rich fractions (like Avicel) due to high yields of levoglucosan (a GC/MS detectable compound) that can be obtained with these feedstocks under well controlled pyrolysis conditions [43].

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References

- [1] ExxonMobil, The Outlook for Energy: A View to 2040. ExxonMobil Report, Exxon Mobil Corporation, 2012, http://www.exxonmobil.com/corporate/files/news_pub.eo2012.pdf (accessed 05.11.13).
- [2] H.B. Goyal, D. Seal, R.C. Saxena, Bio-fuels from thermochemical conversion of renewable resources: a review, *Renew. Sustain. Energy Rev.* 12 (2008) 504–517.
- [3] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Vacuum pyrolysis of softwood and hardwood biomass – comparison between product yields and bio-oil properties, *J. Anal. Appl. Pyrol.* 78 (2007) 104–116.
- [4] P.A.M. Claassen, J.B. van Lier, A.M.L. Contreras, E.W.J. van Niel, L. Sijtsma, A.J.M. Stams, S.S. de Vries, R.A. Weusthuis, Utilization of biomass for the supply of energy carriers, *Appl. Microbiol. Biotechnol.* 52 (1999) 741–755.
- [5] M. Galbe, G. Zacchi, A review of the production of ethanol from softwood, *Appl. Microbiol. Biotechnol.* 59 (2002) 618–628.
- [6] G. Berndes, N. Bird, A. Cowie, Bioenergy, Land Use Change and Climate Change Mitigation. Report for Policy Advisors and Policy Makers, 2010, http://www.globalbioenergy.org/uploads/media/1012_IEA_Bioenergy_-_Bioenergy_land_use_change_and_climate_change_mitigation.01.pdf (accessed 05.11.13).

- [7] C.Q. Dong, Z.F. Zhang, Q. Lu, Y.P. Yang, Characteristics and mechanism study of analytical fast pyrolysis of poplar wood, *Energy Convers. Manage.* 57 (2012) 49–59.
- [8] K.R. Cummer, R.C. Brown, Ancillary equipment for biomass gasification, *Biomass Bioenergy* 23 (2002) 113–128.
- [9] D. Maurant, Z.H. Wang, M. He, X.S. Wang, M. Garcia-Perez, K.C. Ling, C.Z. Li, Malee wood fast pyrolysis: effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil, *Fuel* 90 (2011) 2915–2922.
- [10] M. Garcia-Perez, X.S. Wang, J. Shen, M.J. Rhodes, F.J. Tian, W.J. Lee, H.W. Wu, C.Z. Li, Fast pyrolysis oil malee woody biomass: effect of temperature on the yield and quality of pyrolysis products, *Ind. Eng. Chem. Res.* 47 (2008) 1846–1854.
- [11] M. Garcia-Perez, S. Wang, J. Shen, M. Rhodes, W.J. Lee, C.Z. Li, Effects of temperature on the formation of lignin-derived oligomers during the fast pyrolysis of Malee woody biomass, *Energy Fuel* 22 (2008) 2022–2032.
- [12] Q.A. Lu, C.Q. Dong, X.M. Zhang, H.Y. Tian, Y.P. Yang, X.F. Zhu, Selective fast pyrolysis of biomass impregnated with ZnCl₂ to produce furfural: analytical Py-GC/MS study, *J. Anal. Appl. Pyrol.* 90 (2011) 204–212.
- [13] S. Zhou, M. Garcia-Perez, B. Pecha, S.R.A. Kersten, A.G. McDonald, R.J.M. Westerhof, Effect of the fast pyrolysis temperature on the primary and secondary products of lignin, *Energy Fuel* 27 (2013) 5867–5877.
- [14] B.B. Uzun, A.E. Putun, E. Putun, Composition of products obtained via fast pyrolysis of olive-oil residue: effect of pyrolysis temperature, *J. Anal. Appl. Pyrol.* 79 (2007) 147–153.
- [15] A.V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, *Org. Geochem.* 30 (1999) 1479–1493.
- [16] S.-S. Liaw, Z. Wang, P. Ndegwa, C. Frear, S. Ha, C.-Z. Li, M. Garcia-Perez, Effect of pyrolysis temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas fir wood, *J. Anal. Appl. Pyrol.* 93 (2012) 52–62.
- [17] J.L. Zheng, Bio-oil from fast pyrolysis of rice husk: yields and related properties and improvements of the pyrolysis system, *J. Anal. Appl. Pyrol.* 80 (2007) 30–35.
- [18] A.E. Putun, B.B. Uzun, E. Apaydin, E. Putun, Bio-oil from olive oil industry wastes: pyrolysis of olive residue under different conditions, *Fuel Process. Technol.* 87 (2005) 25–32.
- [19] A. Demirbas, The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis, *Fuel Process. Technol.* 88 (2007) 591–597.
- [20] R.H. He, P. Ye, B.C. English, J.A. Satrio, Influence of pyrolysis condition on switchgrass bio-oil yield and physicochemical properties, *Bioresour. Technol.* 100 (2009) 5305–5311.
- [21] M. Amutio, G. Lopez, M. Artetxe, G. Elordi, M. Olazar, J. Bilbao, Influence of temperature on biomass pyrolysis in a conical spouted bed reactor, *Resour. Conserv. Recycl.* 59 (2012) 23–31.
- [22] S. Zhou, Z. Wang, S.-S. Liaw, C.-Z. Li, M. Garcia-Perez, Effect of sulfuric acid on the pyrolysis of Douglas fir and hybrid poplar wood: Py-GC/MS and TG studies, *J. Anal. Appl. Pyrol.* 104 (2013) 117–130.
- [23] ASTM D1102-84, Standard Test Method for Ash in Wood, ASTM International, West Conshohocken, PA, 2013, <http://dx.doi.org/10.1520/D1102>, www.astm.org
- [24] ASTM D1105-96, Standard Test Method for Preparation of Extractive-Free Wood, ASTM International, West Conshohocken, PA, 2013, <http://dx.doi.org/10.1520/D1105>, www.astm.org
- [25] ASTM D1106-96, Standard Method for Acid Insoluble Lignin in Wood, ASTM International, West Conshohocken, PA, 2013, <http://dx.doi.org/10.1520/D1106>, www.astm.org
- [26] ASTM E1758-01, Standard Test Method for Determination of Carbohydrates in Biomass, ASTM International, West Conshohocken, PA, 2007, <http://dx.doi.org/10.1520/E1758-01R07>, www.astm.org
- [27] S.-S. Liaw, S. Zhou, H. Wu, M. Garcia-Perez, Effect of pretreatment temperature on the yield and properties of bio-oils obtained from auger pyrolysis of Douglas fir wood, *Fuel* 103 (2013) 672–682.
- [28] C. Frear, B. Zhao, J. Ma, Q. Zhao, Anaerobic digestion of whole and lipid-extracted algal biomass from four industrial strains—determination of important methane and nutrient information, in: ASABE Annual International Meeting, Kansas City, MO, 2012.
- [29] StatSoft Inc., Electronic Statistics Textbook, 2013, Tulsa, OK, USA, <http://www.statsoft.com/textbook/> (accessed 05.11.13).
- [30] J.L. Bowyer, R. Shmulsky, J.G. Haygreen, Forest Products and Wood Science: An Introduction, Blackwell Publishing, USA, 2007.
- [31] C.J. Gomez, E. Meszaros, E. Jakab, E. Velo, L. Puigjaner, Therm gravimetry/mass spectrometry study of wood residues and an herbaceous biomass crop using PICA techniques, *J. Anal. Appl. Pyrol.* 80 (2007) 416–426.
- [32] A. Pattiya, J.O. Titiloye, A.V. Bridgwater, Evaluation of catalytic pyrolysis of casava rhizome by principal component analysis, *Fuel* 89 (2010) 244–253.
- [33] A. Khelifa, A. Bensakhria, J.V. Weber, Investigations into the pyrolytic behavior of birch wood and its main components: primary degradation mechanisms, additivity and metallic salt effects, *J. Anal. Appl. Pyrol.* 101 (2013) 111–121.
- [34] D.K. Shen, The Pyrolytic Mechanism of the Main Components in Woody Biomass and Their Interactions, University of Southampton, Faculty of Engineering and the Environment, 2011.
- [35] Y.F. Liao, Mechanism Study of Cellulose Pyrolysis, Zhejiang University, 2003.
- [36] X.F. Zhu, Q. Lu, Production of chemicals from selective fast pyrolysis of biomass, in: M. Momba, F. Bux (Eds.), Biomass, Sciyo, Croatia, 2010.
- [37] M. NikAzar, M.R. Hajaligol, M. Sohrabi, B. Dabir, Mineral matter effects in rapid pyrolysis of beech wood, *Fuel Process. Technol.* 51 (1997) 7–17.
- [38] X. Wang, S.R.A. Kersten, W. Prins, W.P.M. van Swaaij, Biomass pyrolysis in a fluidized bed reactor. Part 2: experimental validation of model results, *Ind. Eng. Chem. Res.* 44 (2005) 8786–8795.
- [39] P.R. Patwardhan, Understanding the Product Distribution from Biomass Fast Pyrolysis (PhD dissertation), Iowa State University, 2010.
- [40] A. Aho, N. Kumar, K. Eranen, B. Holmbom, M. Hupa, T. Salmi, D.Y. Murzin, Pyrolysis of softwood carbohydrates in a fluidized bed reactor, *Int. J. Mol. Sci.* 9 (2008) 1665–1675.
- [41] F. Shafizadeh, R. Furneaux, T.T. Stevenson, T.G. Cochran, Acid-catalysed pyrolytic synthesis and decomposition of 1,4:4,6-dianhydro- α -D-glucopyranose, *Carbohydr. Res.* 61 (1978) 519–528.
- [42] S. Larsson, E. Palmqvist, B. Hahn-Hagerdal, C. Tengborg, K. Stenberg, G. Zacchi, N.O. Nilvebrant, The generation of fermentation inhibitors during dilute acid hydrolysis of softwood, *Enzyme Microb. Technol.* 24 (1999) 151–159.
- [43] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Influence of inorganic salts on the primary pyrolysis products of cellulose, *Bioresour. Technol.* 101 (2010) 4646–4655.